LiBC by Polarized Raman Spectroscopy: Evidence for Lower Crystal Symmetry?

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(Dated: February 1, 2008)

The paper presents polarized Raman scattering study on a few-micron-size crystallite of LiBC with natural faces. The experiment on as grown sample has revealed a four lattice modes with frequencies at 1276 cm^{-1}, 830 cm^{-1}, 546 cm^{-1} and 170 cm^{-1}, respectively. The number of observed Raman lines and their selection rules are incompatible with the assumed D_{6h} symmetry. The modes at 1276 cm^{-1} and 170 cm^{-1} correspond to the expected Raman active modes. In contrast with the superconducting compound MgB_2, the B-C bond stretching mode (at 1276 cm^{-1}) has rather small damping. The two "forbidden" modes (at 830 cm^{-1} and 546 cm^{-1}) disappeared after subsequent thermal treatment.

Recently there were many attempts to further increase the remarkably high phase transition temperature toward the superconducting state in MgB_2[1] by various chemical substitutions and doping, but with very little progress.[2] A new hope was brought by theoretical proposition that in a related isoelectronic compound, LiBC, significantly higher phase transition temperatures can be attained by hole doping produced by Li non-stoichiometry or by field injection technique[2]. Since the spectroscopic information on the phonon spectra in these electron-phonon coupling type superconductors[3,4,5,6,7,8] is obviously important, we have undertaken a basic polarized Raman scattering characterization of both MgB_2[9] and LiBC. The previous polarized Raman study on MgB_2[9] have proven that the unusually broad spectral feature around 600 cm^{-1} corresponds indeed to the E_{2g} zone center mode. The present polarized Raman study complements the recent results on LiBC phonons by infrared spectroscopy[10,11] and ab-initio calculations[12].

According to Ref.[13], the LiBC crystals belongs to the D_{6h}^4 (P6$_3$/mmc) space group symmetry, with Li, B and C atoms in 2a, 2c and 2d Wyckoff positions, respectively. Such structure is thus similar to MgB_2, except for the replacement of Mg by Li and by replacement of B by C at every second position along in-plane covalent bonds as well as along the hexagonal axis, what leads to doubled unit cell along the hexagonal axis. The factor group analysis at the Γ-point yields $2A_{2u} + 2B_{1g} + B_{2u}$ and $2E_{1u} + 2E_{2g} + E_{2u}$ zone center optic modes with atomic displacements parallel and perpendicular to the hexagonal axis, respectively. Because of the unit cell doubling, the internal modes of B-C planes form Davydov-like doublets: one pair of B-C bond stretching modes ($1E_{1u} + 1E_{2g}$) and a pair of ring puckering modes ($1A_{2u} + 1B_{1g}$). The remaining six modes can be understood as "external" modes including a pair of purely Li modes ($1E_{2u} + 1B_{1g}$) and four other modes in which the B-C planes vibrate without deformation. Among all these modes, only the E_{2g} representation is Raman active, so that only two first order Raman modes are to be expected in LiBC.

The experiments were carried out at room temperature, using a Renishaw Raman microscope with 514.5 nm (2.41 eV) argon laser excitation. The instrument allows measurements of polarized Raman spectra in back scattering from a spot size down to 1-2 microns in diameter. To minimize heating of the sample in the laser focus, the laser power was kept below 1mW. We have used the same, about 10 micron thick platelet sample, as in the recent IR reflectivity study[10]. A regular hexagonal flat terrace with a diameter of about 10 microns (see Fig. 1 of the Ref. 10) in the corner of the sample confirms[14] that the hexagonal axis is perpendicular to the platelet sample.

The backscattering cross-polarized spectrum measured directly from this small hexagonal face is shown in the lower curve of the Fig. 1. As expected, there are two sharp Raman lines. Obviously, the higher frequency mode (near 1176 cm^{-1}) corresponds to the E_{2g} bond stretching mode (neighbors in B-C planes vibrate in anti-phase, neighbors along hexagonal axis vibrate in-phase, Li does not participate). It has practically the same frequency as the E_{1u} bond stretching mode (neighbors in B-C planes and neighbors along hexagonal axis vibrate in anti-phase), seen clearly in the IR reflectivity spectra[10]. This shows that the Davydov-like splitting is rather small, in agreement with the ab-initio calculations[12] predicting the two zone center bond stretching modes at[11] 1185 cm^{-1} and 1194 cm^{-1}. Let us note that unlike in MgB_2, both these bond stretching modes in LiBC have rather small damping. Therefore, the electron-phonon interaction properties of LiBC are probably closer to AlB_2.[15,16]

The eigenvector of the second expected E_{2g} mode represents a shear mode of rigid B-C planes (all atoms in B-C plane move in the same sense, the next layer vibrates in anti-phase, Li does not participate). Such mode obviously derives from the transverse acoustic mode at the A-point of the parent MgB_2 structure, so that its frequency can be estimated from the velocity of the transverse acoustic modes propagating along the hexagonal axis. The frequency of the corresponding A-point mode in MgB_2 and AlB_2 can be read from Fig. 3 of Ref. 16 (200 cm^{-1} and 160 cm^{-1} respectively). Indeed, this estimation nicely agrees with the frequency of the other mode (near 170 cm^{-1}) observed in our cross-polarized spectra shown in Fig.1.
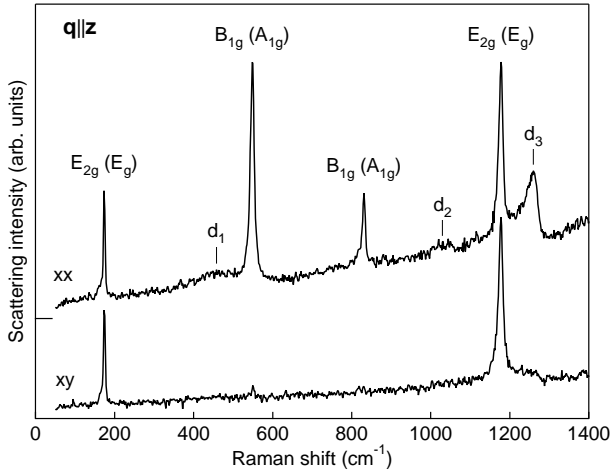
FIG. 1: Polarized Raman spectra taken from the hexagonal terrace on the LiBC single crystal shown in Fig. 1 of Ref.10. The lower curve corresponds to the cross-polarized configuration, the upper one, with a vertical offset shown by the horizontal mark on the vertical axis, corresponds to the parallel-polarized configuration. Labels are explained in the text.

The upper curve in the Fig. 1 was taken from the exactly same spot but with parallel polarization. In agreement with the expected symmetry properties of Raman tensors for the E_{2g} modes, the intensity of the two above discussed modes does not change significantly. At the same time, several new lines have appeared in the spectrum. Somewhat higher luminescence background and broad features d_1, d_2 and d_3 corresponding to the pronounced bands of LiBC phonon density states (see Fig. 3 of Ref. 12, Fig. 4 of Ref. 11) are rather common for parallel-polarized scattering configuration[9]. However, the presence of the two additional sharp lines near 546 cm^{-1} and 830 cm^{-1} is in a flagrant disagreement with the above symmetry analysis, as if the actual factor group symmetry were lower than that of the expected D_{6h} group.

There is no doubt that the 830 cm^{-1} mode is a "ring-puckering" mode. It is too high frequency for an "external" mode and the frequency region of bond stretching modes is limited by the d_2 and d_3 edges of the phonon density of states. Moreover, its frequency roughly coincides with ring-puckering phonon band calculated ab-initio[12].

There are certainly various mechanisms that may be invoked to explain the Raman activity of the ring-puckering mode in as-grown LiBC, but a decisive proof for the actual mechanism is in anyway beyond the scope of this study. Nevertheless, we would like to point out that a rather straightforward explanation can be obtained when assuming that the puckering of B-C planes is in fact present as a static distortion. In this case the puckering mode, which is "frozen in" the parent P6$_3$/mmc structure, becomes a totally symmetric mode

of the distorted structure, and such a mode is always Raman active in parallel-polarized geometry. Since just four clear Raman modes have been observed in our spectra, we have searched possible candidates for frozen-in modes among the zone center modes only. As mentioned previously, there are only two such puckering modes ($1A_{2u} + 1B_{1g}$). We can exclude the A_{2u} mode because it would reduce the factor group symmetry towards C_{6v} (within C_{6v}, the E_{1u} should appear together with the two E_{2g} modes as 3 E_2 modes in the cross-polarized spectra, while only two modes were observed there). Thus, we are left with a single candidate, the B_{1g} mode. The B_{1g} zone center mode distortion leads to the D_{3d}^3 (P$\bar{3}$m1) structure, which is compatible with our experimental data, as we shall show in the following.

First of all, the factor group analysis for the hypothetic distorted structure yields $3A_{2u}+2A_{1g}$ and $3E_u+2E_g$ zone center optic modes with atomic displacements parallel and perpendicular to the trigonal axis, respectively. They are all either Raman ($2A_{1g}$ and $2E_g$) or infrared ($3A_{2u}$ and $3E_u$) active modes. To facilitate further discussion, from now on we distinguish the symmetry adapted eigenvectors by the symbols of correspondent irreducible representation in both D_{6h} and D_{3d} factor groups, the latter being in the parentheses.

The observation shown in the Fig. 1 is in agreement with the Raman selection rules for the D_{3d} factor group. The pair of $B_{1g}(A_g)$ modes should be observable in parallel-polarized but not in cross-polarized geometry, which indeed holds for the lines near 546 cm^{-1} and 830 cm^{-1}. The requirement that the pair of $E_{2g}(E_g)$ modes should be observable in both cross-polarized and parallel-polarized geometry with the same intensity holds both for D_{3d} and D_{6h}) symmetry (and is thus also fulfilled).

Measurements analogous to those shown in the Fig. 1 were reproduced at several places in the sample, both inside and outside the small hexagonal terrace, and for different orientations of incident light polarization axis, all with similar result. To obtain one more supplementary argument in favor of our conclusion, we have tried to measure the remaining polarization components from backscattering on the edges of the sample. Unfortunately, we have not found well developed flat surfaces perpendicular to the platelet, so that this measurement was rather difficult and the phonon propagation direction may not be strictly perpendicular to the c-axis. Nevertheless, the obtained results are again in agreement with the proposed assignment within the D_{3d} factor group. The pair of $E_{2g}(E_g)$ modes is present even when one of the polarization axes is parallel to the hexagonal (trigonal) axis (see "zz" and "zx" spectra shown in Fig. 2), which is expected within D_{3d} but not allowed in D_{6h}. Similarly, the $B_{1g}(A_g)$ modes, are missing in cross-polarized geometry, as required by D_{3d} group Raman selection rules. Finally, no frequency shifts which could appear in the case of polar modes due to the LO-TO splitting were observed, again in agreement with our
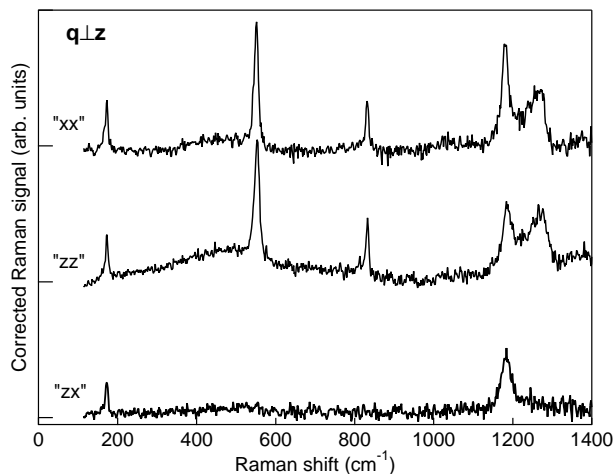
FIG. 2: Polarized Raman spectra taken from the edge of the LiBC single crystal shown in Fig. 1. of Ref.10. For clarity, luminescence background was subtracted, the vertical offset is shown by the horizontal marks on the vertical axis. The labels "xx", "zz", "xz" denotes incident and scattered polarizations (z and x stands for polarization along and perpendicular to the trigonal axis, respectively.)

above conjecture that the frozen displacement is not the A_{2u} polar mode.

Samples of the same origin were previously studied by infrared spectroscopy.[10] Among the six remaining zone center optic modes, three have dipole moment along the trigonal axis $(2A_{2u}(A_{2u}) + 1B_{2u}(A_{2u}))$ and three have dipole moments perpendicular to the trigonal axis $(2E_{1u}(E_u) + 1E_{2u}(E_u))$. The latter triplet should contribute in the infrared reflectivity, measured from the large surface of the investigated sample. This is in agreement with the measurements of Ref. 10, which shows a clear B-C stretching mode near 1180 cm^{-1} (this has to be $E_{1u}(E_u)$ mode) and a broad band with two well defined peaks (which could be tentatively assigned to the remaining $E_{1u}(E_u) + E_{2u}(E_u)$ modes).

After completing of the above described investigations, the sample was placed in a variable-temperature cell (LINKAM) in a hope to drive the system across a hypothetic phase transformation towards the prototype $P6_3/mmc$ structure by thermal treatment. For this reason, the sample was first cooled down to about 80 K and then heated up in steps of about 50 K in order to see the evolution of the Raman spectrum. There was no clear indication of such a phase transformation up to 400 K.

Unfortunately, in the vicinity of 450 K, a sudden dropout of electricity stopped the experiment. Continuation of the experiment was possible two days later. This time the measurements were done while heating the sample from the room temperature up to 650 K. To our surprise, the two forbidden lines were never observed again.

In conclusion, we have observed scattering by the two E_{2g} LiBC Raman active modes (at 1276 cm^{-1}, and 172 cm^{-1}, respectively). The relatively high frequency and small damping of the stretching mode correlates[12] with the absence of the superconductivity in the stoichiometric LiBC. This indicates that the Raman scattering provides a very useful tool for easy testing of MgB$_2$ related superconducting materials.

We have found that results of the polarized Raman measurements on the as-grown LiBC single crystal are incompatible with the assumed LiBC structure. Most unexpectedly, we have found two other modes at 830 cm^{-1} and 546 cm^{-1}. The former forbidden mode is probably the B_{1g} B-C puckering mode. The observed results can be explained assuming lower crystal symmetry, e.g $P\bar{3}m1$ space group symmetry induced by puckering displacement of B-C planes. This need not be the correct picture (ab-initio test calculations have not found such puckered structure stable[17]), but it nevertheless gives some insight into the phenomenon.

The two forbidden Raman modes vanished after a subsequent thermal treatment. The influence of thermal treatment of LiBC based materials seems to be of essential importance for their superconductor properties, and the appearance (and disappearance) of forbidden Raman lines in LiBC samples may be one of the clue in understanding of the relevant microscopical processes. For example, B-C order stacking faults and/or Li non-stoichiometry allows a number of possible scenarios. Obviously, detailed understanding calls for further investigations. It seems that the sample is sensitive to heating to temperatures exceeding 400 K. We plan to perform Raman investigations of the thermal treatment in LiBC on new samples in future.

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